

SUPPORTING INFORMATION

Controllable Expansion of Single-Walled Carbon Nanotube Dispersions

Using Density Gradient Ultracentrifugation

Pei Zhao, Erik Einarsson, Rong Xiang, Yoichi Murakami, Shigeo Maruyama

I. EXPERIMENTAL DETAILS

Sample layer:

7.5 mg ACCVD-SWNTs were dispersed in 6 mL D₂O containing 0.5% w/v (0.03g) *sodium deoxycholate* (DOC). The dispersion was then bath sonicated for 10 min, followed by horn ultrasonication for 1 hour (UP-400s, Hielscher Ultrasonics, 1 cycle, 400 W). The suspension was put into 4.5 mL glass centrifuge tubes (1.4 mL each, total amount is 5.6 mL, some of the suspension may vaporize during ultrasonication), then ultracentrifuged at 78 krpm (276,000 g) at 22 °C (Hitachi CS 100GXL) for 15 min, using an angle rotor (Hitachi-Koki S100AT), both acceleration and deceleration values were set to 9 (maximum). The upper portion of the supernatant was taken (0.875 mL from each tube, total amount is 3.5mL), and mixed with 3.5 mL of 60% iodixanol and 0.07 g *sodium dodecyl sulfate* (SDS), and then horn ultrasonicated for another 30 min. At this time the DOC concentration in the sample layer is 0.25% w/v.

Density gradient:

Density gradient layers of 20, 30, and 40% concentration were prepared with 1.5% w/v SDS each and bath sonicated them for 1 hour. Using plastic test tubes (5mL), a 40% layer was put at the bottom, followed by a 30% layer and then a 20% layer on top of that. The upper layers were both deposited drop by drop so as to minimize mixing. The tubes were then sealed, and laid horizontally for 1 hour to make a continuous density gradient.

Ultracentrifugation process:

Using a syringe needle, 1.5 mL of the SWNT dispersion was added into each density gradient tube (within the 30% iodixanol layer). The capsules were then placed in a swing rotor (Hitachi-Koki S52ST), and ultracentrifuged at 52 krpm (197,000g) at 15 °C for 22 hours. In this case the acceleration and deceleration value was set to five.

Controllable overall expansion:

During the preparation of the inserted sample layer, which contains equal volumes of unbundled SWNT dispersion and 60% iodixanol, the amount of SDS that contained in this layer was either 0% (no SDS), 1%, 1.25%, or 1.5% w/v. Insertion of this layer was followed by 1 hour of horn-type ultrasonication. All other DGU parameters were kept the same as in the previous section. Results are shown in Figure S5. Our hypothesis is that DOC packs in higher density on small diameter SWNTs, leaving less open space for subsequent SDS binding than is available on large diameter SWNTs. In this case, increased SDS concentration leads to more SDS binding to large diameter nanotubes, which increases their densities and drives them further down the density gradient (as seen in Fig. S5). Small diameter SWNTs, however, are relatively unaffected by the SDS concentration.

HiPCO/CoMoCAT SWNTs DGU preparation:

3.0 mg HiPCO/CoMoCAT-SWNTs were dispersed in 6 mL D₂O containing 0.5% w/v DOC. The dispersion was then bath sonicated for 10 min, followed by horn ultrasonication for 1 hour. The suspension was then ultracentrifuged at 78 krpm (276,000 g) at 22 °C (Hitachi CS 100GXL) for 30 min using an angle rotor. The following procedures are identical to the ACCVD-SWNTs DGU preparation. Results shown in Figure S6.

Fraction collection:

A micro-pipette was used to fractionate the final dispersion, which was taken out in 20 µL sections. Each fraction was diluted to a concentration appropriate for subsequent spectroscopic analysis.

Spectroscopy:

D₂O containing 0.1% w/v DOC and 1.33% w/v SDS was used as the baseline of UV-Vis-NIR absorbance (UV-3150, Shimadzu). Samples were also characterized by photoluminescence excitation (PLE, Fluorolog, HORIBA) and TEM (JEOL 2000EX, operated at 120 kV).

II. SUPPORTING FIGURES

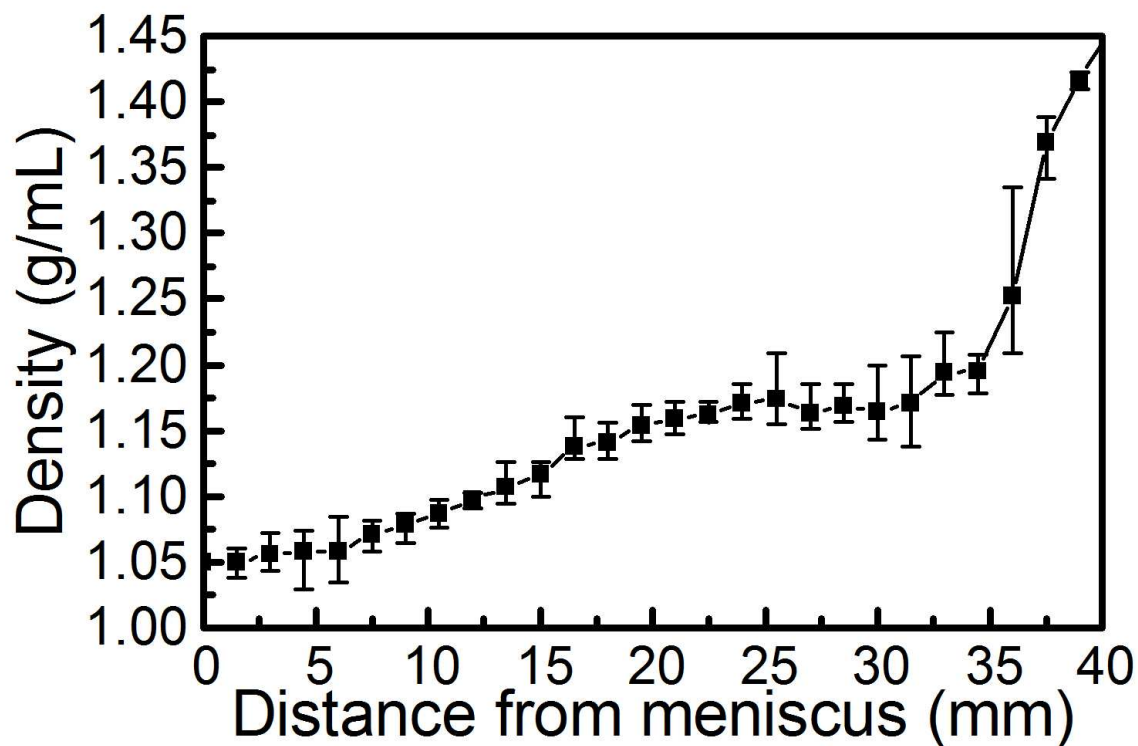


Figure S1. Density gradient distribution after ultracentrifugation. The volume of each layer is 150 μ L.



Figure S2. Density gradient fractions with different colors, with mm scale bar (zero is at bottom of the meniscus).

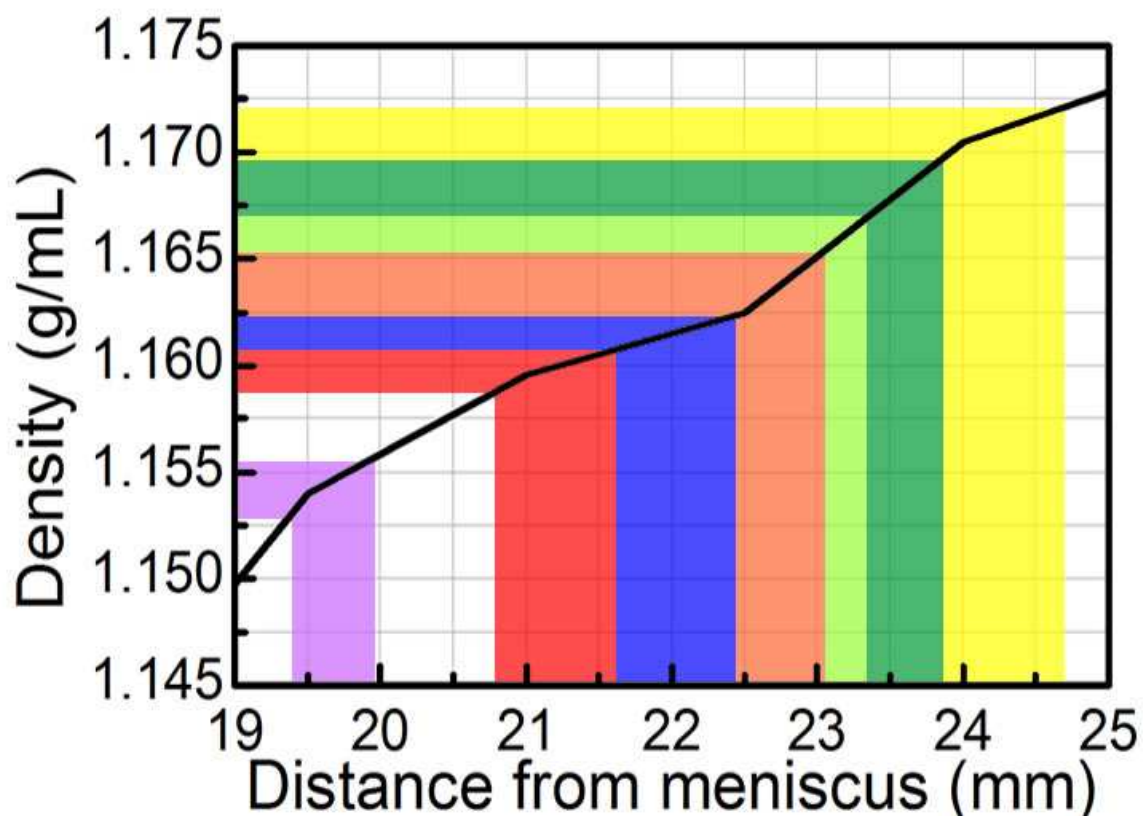


Figure S3. Colored fractions and their corresponding densities in the DGU tube.

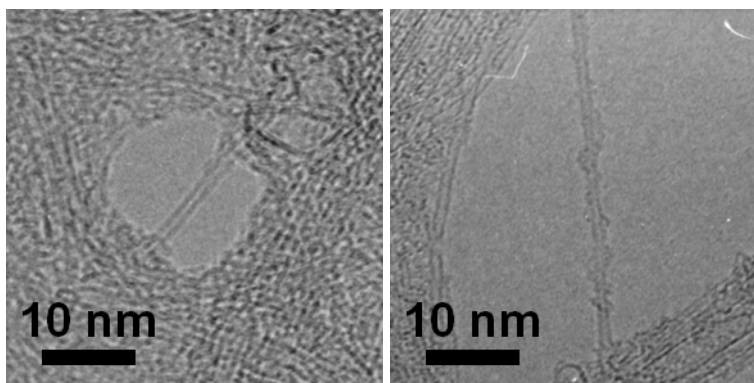


Figure S4. Transmission electronic microscopy images of SWNTs extracted from the violet fraction. The sample was rinsed thoroughly prior to observation to remove as much iodixanol as possible.

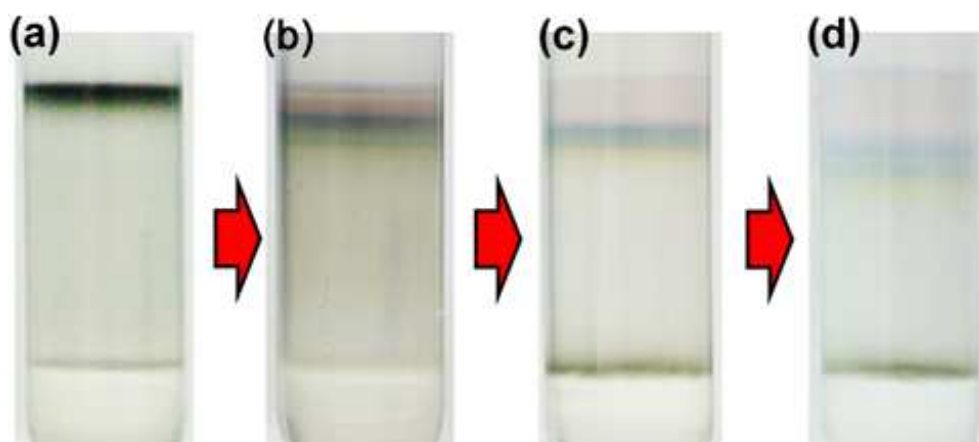


Figure S5. Controllable overall expansion of layers by adjusting surfactant concentration. Concentrations of SDS are (a) 0.0%, (b) 1.0%, (c) 1.25%, and (d) 1.5% respectively.

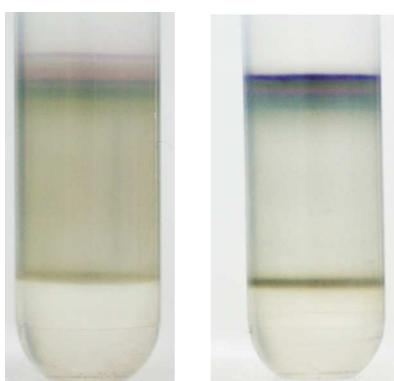


Figure S6. Expansion of HiPCO (left) and CoMoCAT (right) SWNTs. A highly concentrated violet (6,5) layer is apparent in the CoMoCAT expansion.

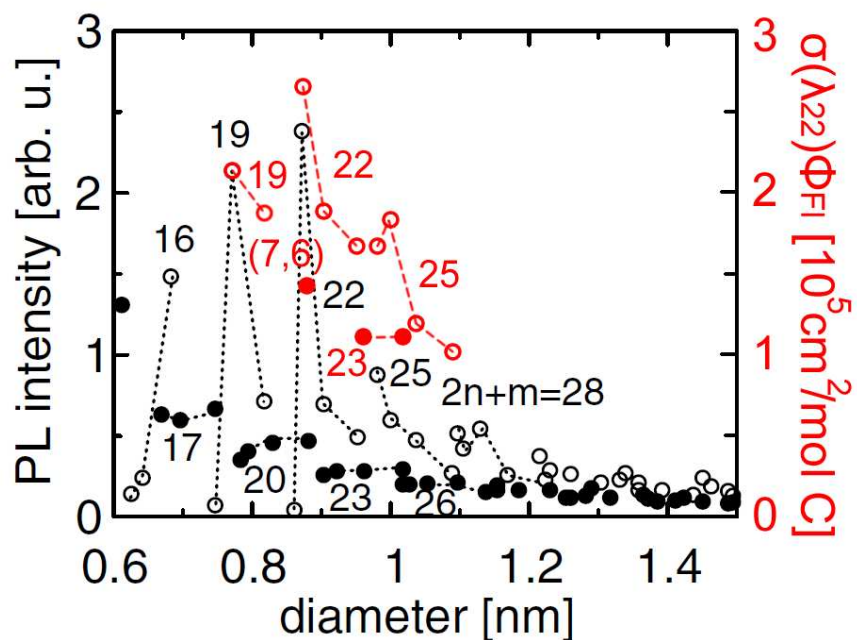


Figure S7. Comparison of SWNT calculated PL intensities from Ref. [24] (black) and PL action cross sections from Ref. [25] (red). Type I and type II are denoted by open and solid dots, respectively.

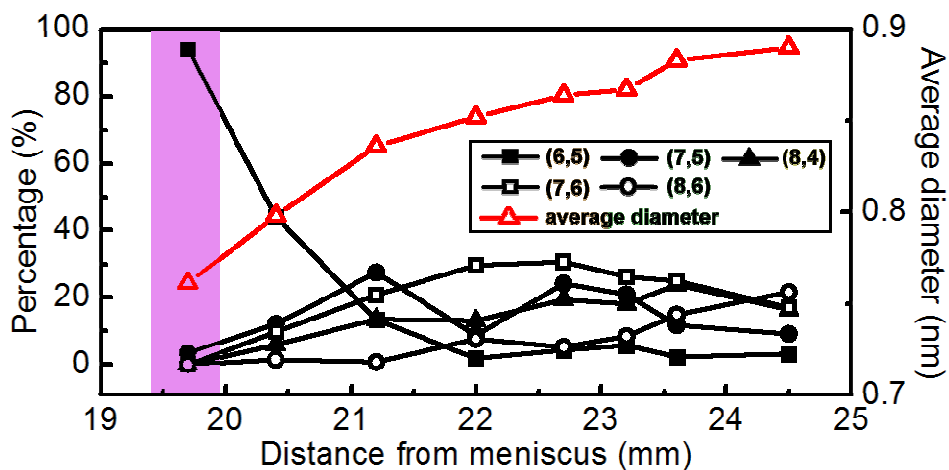


Figure S8. Abundance of dominantly selected (n,m) semiconducting nanotube species and their average diameters in the resulting colored fractions. Percentages were calculated from experimental PLE intensities normalized by theoretical PLE intensities [24].